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Material properties

Thermoplastic starch/poly(lactic acid) sheets coated with cross-linked chitosan

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ABSTRACT

Blends of thermoplastic starch (TPS) and poly(lactic acid) (PLA) (70/30 TPS/PLA wt/wt) were thermopressed to produce biodegradable sheets. These sheets were coated with cross-linked chitosan by two different methods: spraying and immersion. The coated sheets presented a more irregular surface than uncoated samples, which was associated with the chitosan reticulation. The chitosan coating reduced the water solubility and the water vapor permeability of the sheets due to being less hygroscopic. Coated sheets were more rigid and had higher tensile strength than uncoated sheets, because the cross-linking joins the macromolecules covalently, reducing the mobility of the chains. Higher glycerol concentration in the TPS increased the elongation at break due to the glycerol plasticizing effect. Coating by spraying was more effective at changing the sheet properties than coating by immersion, and this technique can be used to reduce the hydrophilic character of biodegradable films, allowing their use as packaging materials.

1. Introduction

Currently, there is great interest in biodegradable polymers obtained from renewable resources, such as starch, to replace conventional polymers of petrochemical origin in several applications, for instance, the production of flexible and semi-rigid materials.

Thermoplastic starch materials (TPS), due to their hydrophilic character, have high water vapor permeability and their mechanical properties are dependent on the relative humidity, thus limiting their use on an industrial scale [1, 2]. Blends of TPS with other biodegradable polymers represent an alternative to improve the properties of thermoplastic starch materials [3, 4, 5].

Avérous and Fringant [3] tested starch blends with different polyesters. In the presence of polyesters the mechanical properties and dimensional stability increased, while the hydrophilic character of the starch decreased. Yokesahachart and Yoksan [6] studied TPS blends with poly(lactic acid), and both the mechanical properties and processability of the blend improved with higher concentrations of PLA. Ke and Sun [7] studied TPS/PLA blends and evaluated the effect of the initial moisture content of the starch (0 to 40%) on the thermal and mechanical properties. The authors observed that moisture did not significantly affect the mechanical properties and transition temperatures of the blends. On the other hand, on increasing the starch moisture in the blends, an increase in water absorption was observed. In a previous study [8], our research group produced films from TPS/PLA blends (90:10, 80:20 and 70:30 w:w) and there was an increase in tensile strength and reduction in water vapor permeability with increasing concentration of PLA.

Several studies have shown that coatings improve the mechanical properties and water vapor barrier of starch films [9, 10]. Ryu et al. [11] coated starch films by immersion in zein solution. The films were mechanically stronger and showed lower water solubility than films without zein, because zein is more hydrophobic than starch. Bangyekan

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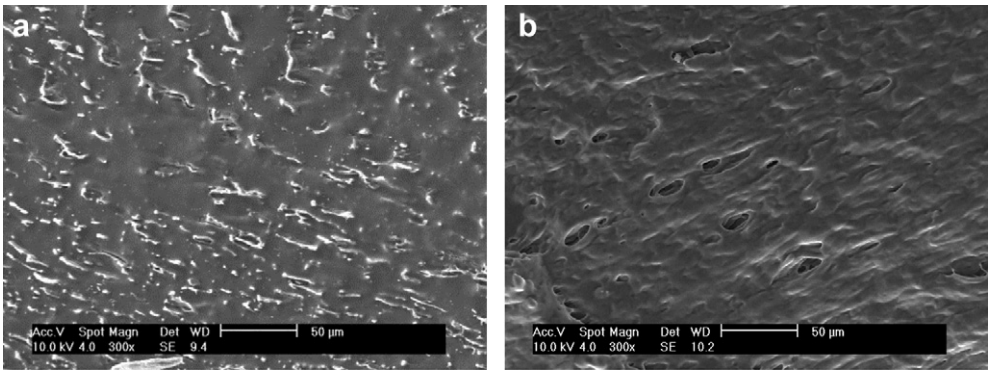

Fig. 1. SEM fracture micrographs of TPS25/PLA blend sheets (a) and the blend sheets of TPS25/PLA previously immersed in chloroform for 24h (b).

et al. [12] coated starch films with chitosan and observed an improvement in the mechanical and water vapor barrier properties, reducing the wettability and water sorption.

The objective of this study was to produce biodegradable sheets of TPS and PLA coated with cross-linked chitosan and to study the effect of coating on their mechanical properties, water solubility and water vapor permeability.

2. Material and methods

2.1. Materials

Native cassava starch (amylose 20.8±0.6 wt%) was obtained from Indemil (Brazil), poly(lactic acid) (PLA) was supplied by Cargill (Natureworks LLC, USA) under the brand name Ingeo 3251D, and chitosan (medium molecular weight, 75-85% deacetylated) was purchased from Sigma–Aldrich (USA). Glycerol was supplied by Dinâmica (Brazil) and glutaraldehyde by Nuclear (Brazil).

2.2. Preparation of sheets

Initially, pellets of thermoplastic starch were produced by extrusion in concentrations of 0.25 g and 0.30 g of glycerol per 1 g of starch (TPS25 and TPS30, respectively). The pellets of TPS and PLA were then mixed at a ratio of 70/30 (wt/wt) and extruded to obtain blends of TPS25/PLA and TPS30/PLA. Both the TPS and the blends were processed in a single-screw extruder (BGM, model EL-25, Brazil) with 25 mm screw diameter and L/D ratio of 30. The screw speed was 35 rpm and the temperatures in the four heating zones were 120°C and 150°C for the TPS and blend processing, respectively.

For the sheet production, blend pellets were thermopressed in a hydraulic press (Schulz, model PHS, Brazil) at 150°C and 2.6 MPa and then cooled to room temperature.

2.3. Coating

The coating solution was prepared by dissolving 0.1% (w/v) of chitosan in an aqueous solution of 1% acetic acid (v/v). The coating of the sheets was carried out by two methods: (i) spraying the solution onto the sheet; and (ii) immersing the sheet in the chitosan solution. The cross-linking was carried out with an aqueous solution of 0.5% glutaraldehyde (v/v) for spraying in process (i) and immersion in process (ii), and the samples were then dried with hot air. Coated sheets were kept in an air flow at room temperature for 24h. In some cases, as previously mentioned, the procedure for the deposition of the chitosan film and subsequent cross-linking was repeated, these samples being denoted as “Spray (2x)” and “Immersion (2x)”. The uncoated sheets are considered as the control.

2.4. Characterization of the sheets

2.4.1. Scanning electron microscopy (SEM)

Images of sample surfaces and fractures were obtained using a Philips XL-30 scanning electron microscope (USA) for morphological analysis of the sheets. The samples were coated with a fine gold layer using a sputter coater model SCD 050 (BAL-TEC, USA) before obtaining the micrographs.

2.4.2. Water solubility

The solubility of the sheets in water was defined as the dry matter content that was solubilized after 24h of immersion in water at 25°C. Measurements were carried out on three replicates using the methodology described by Irissin-Mangata et al. [13], with some adjustments.

2.4.3. Water vapor permeability

The water vapor permeability of the laminates was determined in appropriate diffusion cells, using a relative humidity (RH) of 2% inside the cell and 75% outside the cell (ASTM E 96 - 00) [14]. All tests were conducted in triplicate.

2.4.4. Tensile testing

Tensile tests were performed using an EMIC DL 2000 analyzer (EMIC, Brazil), according to the standard method ASTM D 882 - 02 [15]. The elasticity modulus, tensile strength and elongation at break were calculated from the stress–strain curves considering the results of at least ten tests for each sample.

2.4.5. Statistical analysis

Statistica software (Oklahoma, USA) version 8.0 was used for all statistical analysis. Analysis of variance (ANOVA) and the Tukey test for comparison of means were

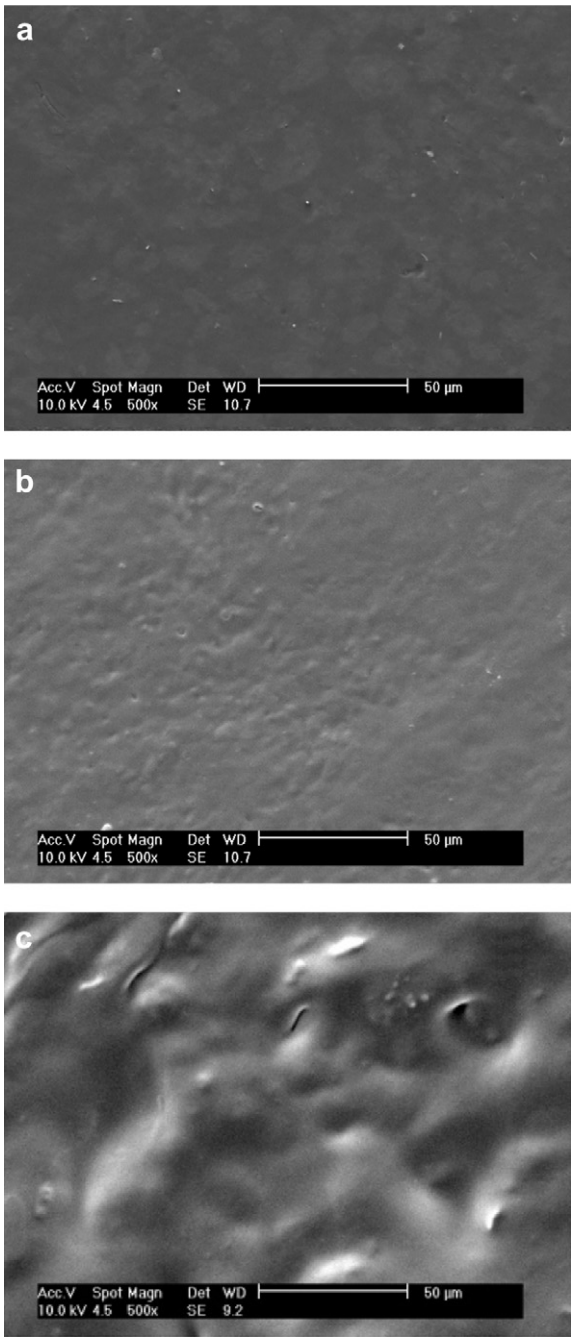

Fig. 2. SEM surface micrographs of TPS25/PLA blend sheets uncoated (a) and coated with cross-linked chitosan using spraying (b) or immersion (c).

applied in the experimental data analysis. The significance level used was $p < 0.05$.

3. Results and discussion

The sheets produced from blends of thermoplastic starch and poly(lactic acid) had good processability during molding. The sheets showed good handleability and homogeneous appearance, without apparent cracks. The cross-linked chitosan deposited onto sheets homogeneously overlaid the surfaces without changing the appearance of the sheets, and its presence did not change the thickness, which was around 0.9-1.2 mm.

3.1. Scanning electron microscopy

Micrographs were obtained of sheets previously immersed in chloroform for 24h in order to solubilize the PLA and allowed observation of PLA regions in the TPS matrix. Images were also taken of sheets not immersed in chloroform. Fig. 1(a) shows the fracture micrograph of the TPS25/PLA sheet (section 2.2) and Fig. 1(b) shows the sheet previously immersed in chloroform. In Fig. 1(a) it is possible to observe the PLA domains (lighter) distributed in the TPS matrix (darker). Fig. 1(b) shows the voids previously occupied by PLA domains, characterizing the immiscibility between the PLA and TPS. This behavior is associated with the difference between the hygroscopicity of starch (hydrophilic) and PLA (hydrophobic). These findings verify the observations of a previous study of Müller et al. [8].

Fig. 2 shows the surface micrographs of the TPS25/PLA sheet uncoated (Fig. 2a), and coated by spraying (Fig. 2b) or by immersion (Fig. 2c) with cross-linked chitosan. Regardless of the coating process, the micrographs indicate a continuous covering of chitosan on the sheet surface.

Coating the sheets with chitosan led to a higher surface roughness compared with the uncoated sheets, independently of the method used for coating. This feature may be associated with the reaction of glutaraldehyde with repeating units of the chitosan polymer chain due to the cross-linking process. Furthermore, the sheets coated by immersion showed a more irregular surface than the spray-coated samples, probably because the immersion favored water diffusion into the starch matrix which modifies the surface appearance of the sheet.

Gierszewska-Drużyńska and Ostrowska-Czubenko [16] studied the ionic cross-linking of chitosan membranes with sodium tripolyphosphate and observed the surface of the films by SEM. They reported that the surface of the chitosan films was smooth, while on the surface of the cross-linked chitosan membrane there were numerous visible lumps. These differences in the surface morphology were confirmed by AFM, with calculated values for surface roughness of 3.56 and 23.71 nm for the uncross-linked and cross-linked chitosan films, respectively.

3.2. Water solubility

Due to the hydrophilic characteristic of the TPS matrix, the water solubility is an important parameter in terms of the practical application of these materials, and the results obtained are presented in Table 1.

The uncoated TPS25/PLA and TPS30/PLA sheets showed no significant difference in water solubility, in other words, the glycerol concentration in the blend did not affect the solubility of the sheets, probably due to the effect of the PLA incorporation.

Table 1
Water solubility of the TPS / PLA sheets with and without cross-linked chitosan coating.

Coating process	Solubility (%)	
	TPS25/PLA	TPS30/PLA
Control	$33.6 \pm 1.3^{b\text{-}A}$	$35.2 \pm 0.7^{d\text{-}A}$
Spray	$13.8 \pm 0.2^{a\text{-}A}$	$12.8 \pm 1.2^{a\text{-}A}$
Spray (2x)	$13.8 \pm 0.4^{a\text{-}A}$	$13.9 \pm 0.8^{a,b\text{-}A}$
Immersion	$14.3 \pm 0.1^{a\text{-}A}$	$16.1 \pm 0.2^{c\text{-}B}$
Immersion (2x)	$14.0 \pm 0.5^{a\text{-}A}$	$15.4 \pm 0.3^{b,c\text{-}B}$

Note: Mean ± standard deviation. Means with different lower case letters in the same column or means with different capital letters in the same row designate difference at the 0.05 level according to the Tukey test.

Table 2
Water vapor permeability of TPS/PLA sheets with and without cross-linked chitosan coating.

Coating process	Permeability $(m.g.h^{-1}.Pa^{-1}.m^{-2}) \times 10^6$	
	TPS25/PLA	TPS30/PLA
Control	$1.8 \pm 0.2^{b\text{-}A}$	$1.8 \pm 0.1^{b\text{-}A}$
Spray	$1.2 \pm 0.1^{a\text{-}A}$	$1.8 \pm 0.1^{b\text{-}B}$
Spray (2x)	$1.3 \pm 0.1^{a\text{-}A}$	$1.7 \pm 0.2^{b\text{-}B}$
Immersion	$1.5 \pm 0.3^{a,b\text{-}A}$	$1.6 \pm 0.3^{a,b\text{-}A}$
Immersion (2x)	$1.4 \pm 0.2^{a,b\text{-}A}$	$1.2 \pm 0.1^{a\text{-}A}$

Note: Mean ± standard deviation. Means with different lower case letters in the same column or means with different capital letters in the same row designate difference at the 0.05 level according to the Tukey test.

The sheets coated with cross-linked chitosan were less soluble in water when compared with uncoated sheets, independently of the procedure applied, since the coating reduced the rate of dissolving of the starch, due to its hydrophobic character. The spray method reduced, to a greater extent, the solubility of the sheets (58 %) in relation to the immersion method, since the cross-linked chitosan covering produced by spraying formed a more efficient barrier. Thiré et al. [9] produced coated starch films using the cold plasma technique to reduce the film hydrophilicity and observed a reduction of up to 82% in the water sorption of the coated films, suggesting that this treatment reduces the hydrophilic nature of the film and that the coating acted as a physical barrier to water sorption.

3.3. Water vapor permeability

Table 2 shows the data for water vapor permeability of the TPS/PLA sheets with and without coating with cross-linked chitosan.

There was no difference in the water vapor permeability of the uncoated TPS25/PLA and TPS30/PLA sheets, i.e., the glycerol concentration in the blend did not affect the permeability of the sheets, as also observed for the solubility. This behavior may be due to the presence of PLA, which stabilized the water vapor barrier properties of these materials.

The spray-coated TPS25/PLA sheets presented around 35% lower permeability than the uncoated sheet. The permeability of TPS30/PLA sheets, with and without coating, showed no differences except for the sheet coated by immersion (2x).

The process of water molecule permeation through the sheet occurs via the simultaneous effects of the solubilization process and the diffusion of water molecules in the polymeric matrix. Thus, a reduction in the permeability was expected for the chitosan coated sheets due to a reduction in the overall solubility and diffusion coefficients, since chitosan has a hydrophobic character. However, only a few sheets showed a significant difference.

3.4. Mechanical tests

The TPS25/PLA sheets had higher tensile strength and elastic modulus values than the TPS30/PLA sheets, regardless of the coating procedure used (Table 3). As TPS is the component in higher concentration in the blend, this behavior is due to the greater amount of plasticizer in the TPS30/PLA blend. According to the literature, the plasticizing effect of glycerol on the amylose and amylopectin chains reduces the tensile strength and rigidity of the films [17, 18, 19].

The cross-linked chitosan coating increased both the tensile strength and the elastic modulus, and reduced the elongation at break of the sheets when compared with the control sheet. With the cross-linking of the coating, the macromolecules are covalently linked, forming a three-dimensional network and reducing the mobility of the chains, which makes the sheets less flexible and more resistant. Kittur et al. [20] reported that cross-linked chitosan films showed an 18% reduction in elongation and 33% increase in tensile strength when compared to non-cross-linked films.

TPS30/PLA sheets showed no difference in mechanical properties as a function of the coating process. TPS25/PLA sheets coated by spraying (2x) had a higher tensile strength (3.7 MPa) and elastic modulus (422 MPa) and lower elongation (2.6%) than the samples coated by immersion (2x).

Table 3
Tensile strength, elongation at break and elastic modulus of the TPS/PLA sheets with and without cross-linked chitosan coating.

Coating process	Tensile Strength (MPa)		Elongation at break (%)		Elastic modulus (MPa)	
	TPS25/PLA	TPS30/PLA	TPS25/PLA	TPS30/PLA	TPS25/PLA	TPS30/PLA
Control	$1.7 \pm 0.1^{a\text{-}B}$	$1.0 \pm 0.1^{a\text{-}A}$	$19.2 \pm 2.2^{c\text{-}A}$	$17.2 \pm 6.1^{b\text{-}A}$	$60 \pm 9^{a\text{-}B}$	$32 \pm 7^{a\text{-}A}$
Spray (2x)	$3.7 \pm 0.5^{c\text{-}B}$	$1.6 \pm 0.2^{b\text{-}A}$	$2.6 \pm 0.5^{a\text{-}A}$	$9.1 \pm 1.8^{a\text{-}B}$	$422 \pm 23^{c\text{-}B}$	$72 \pm 14^{b\text{-}A}$
Immersion (2x)	$2.8 \pm 0.4^{b\text{-}B}$	$1.6 \pm 0.2^{b\text{-}A}$	$5.5 \pm 1.4^{b\text{-}A}$	$10.4 \pm 1.7^{a\text{-}B}$	$214 \pm 56^{b\text{-}B}$	$67 \pm 13^{b\text{-}A}$

Note: Mean ± standard deviation. Means with different lower case letters in the same column or means with different capital letters in the same row designate difference at the 0.05 level according to the Tukey test.

4. Conclusions

The coating of TPS/PLA sheets with cross-linked chitosan improved the mechanical and water vapor barrier properties and reduced the water solubility in addition to changing the morphological characteristics of the sheet surface. The coating by spraying was more effective in terms of modifying the sheet properties than immersion. Thus, the spray technique can be used to reduce the hydrophilic character of biodegradable films, allowing their use as packaging materials for different products.

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References

[1] C.M. Chaléat, P.J. Halley, R.W. Truss, Properties of a plasticized starch blend. Part 1: Influence of moisture content on fracture properties, Carbohydrate Polymers 71 (2008) 535–543.
[2] C.M.O. Müller, F. Yamashita, J.B. Laurindo, Evaluation of the effects of glycerol and sorbitol concentration and activity on the barrier properties of cassava starch films through a solubility approach, Carbohydrate Polymers 72 (2008) 82–87.
[3] L. Avérous, C. Fringant, Association between plasticized starch and polyesters: Processing and performances on injected biodegradable systems, Polymer Engineering and Science 41 (2001) 727–734.
[4] R.P.H. Brandelero, M.V.E. Grossmann, F. Yamashita, Effect of the method of production of blends on mechanical and structural properties of biodegradable starch films produced by blown extrusion, Carbohydrate Polymers 86 (2011) 1344–1350.
[5] L. Yu, K. Dean, L. Li, Polymer blends and composites from renewable resources, Progress in Polymer Science 31 (2006) 576–602.
[6] C. Yokesahachart, R. Yoksan, Effect of amphiphilic molecules on characteristics and tensile properties of thermoplastic starch and its blends with poly(lactic acid), Carbohydrate Polymers 86 (2011) 22–31.
[7] T. Ke, X. Sun, Effects of moisture content and heat treatment on the physical properties of starch and poly(lactic acid) blends, Journal of Applied Polymer Science 81 (2001) 3069–3082.
[8] C.M.O. Müller, A.T.N. Pires, F. Yamashita, Characterization of thermoplastic starch/poly(lactic acid) blends obtained by extrusion and thermopressing, Journal of Brazilian Chemical Society 23 (2012) 426–434.
[9] R.M.S.M. Thiré, R.A. Simão, P.J.G. Araújo, C.A. Achete, Redução da hidrofilicidade de filmes biodegradáveis à base de amido por meio de polimerização por plasma, Polímeros 14 (2004) 57–62.
[10] J. Behnisch, J. Tyczkowski, M. Gazicki, I. Pela, A. Holländer, R. Ledzion, Formation of hydrophobic layers on biologically degradable polymeric foils by plasma polymerization, Surface and Coatings Technology 98 (1998) 872–874.
[11] S.Y. Ryu, J.W. Rhim, H.J. Roh, S.S. Kim, Preparation and physical properties of zein-coated high-amylose corn starch film, LWT - Food Science and Technology 35 (2002) 680–686.
[12] C. Bangyekan, D. Aht-Ong, K. Srikulkit, Preparation and properties evaluation of chitosan-coated cassava starch films, Carbohydrate Polymers 63 (2006) 61–71.
[13] J. Irissin-Mangata, G. Bauduin, B. Boutevin, N. Gontard, New plasticizers for wheat gluten films, European Polymer Journal 37 (2001) 1533–1541.
[14] ASTM E 96 – 00, Standard test methods for water vapor transmission of materials (2000).
[15] ASTM D 882 – 02, Standard test methods for tensile properties of thin plastic sheeting (2002).
[16] M. Gierszewska-Drużyńska, J. Ostrowska-Czubenko, Influence of crosslinking process conditions on molecular and supermolecular structure of chitosan hydrogel membrane, Progress in the Chemistry and Application of Chitin and its Derivatives XVI (2011) 15–22.
[17] V.D. Alves, S. Mali, A. Beléia, M.V.E. Grossmann, Effect of glycerol and amylose enrichment on cassava starch film properties, Journal of Food Engineering 78 (2007) 941–946.
[18] Y.P. Chang, A.A. Karim, C.C. Seow, Interactive plasticizing-antiplasticizing effects of water and glycerol on the properties of tapioca starch films, Food Hydrocolloids 20 (2006) 1–8.
[19] S. Mali, F. Sakanaka, F. Yamashita, M.V.E. Grossmann, Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect, Carbohydrate Polymers 60 (2005) 283–289.
[20] F.S. Kittur, K.R. Kumar, R.N. Tharanathan, Functional packaging properties of chitosan films, Z Lebensm Unters Forsch A 206 (1998) 44–47.